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Micropollutant Sorption to Membrane Polymers: A Review of Mechanisms for Estrogens

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Abstract

Organic micropollutants such as estrogens occur in water in increasing quantities from predominantly anthropogenic sources. In water such micropollutants partition to surfaces such as membrane polymers but also any other natural or treatment related surfaces. Such interactions are often observed as sorption in treatment processes and this phenomenon is exploited in activated carbon filtration, for example. Sorption is important for polymeric materials and this is used for the concentration of such micropollutants for analytical purposes in solid phase extraction. In membrane filtration the mechanism of micropollutant sorption is a relative new discovery that was facilitated through new analytical techniques. This sorption plays an important role in micropollutant retention by membranes although mechanisms of interaction are to date not understood. This review is focused on sorption of estrogens on polymeric surfaces, specifically membrane polymers. Such sorption has been observed to a large extent with values of up to 1.2 ng/cm^2 measured. Sorption is dependent on the type of polymer, micropollutant characteristics, solution chemistry, membrane operating conditions as well as membrane morphology. Likely contributors to sorption are the surface roughness as well as the microporosity of such polymers. While retention – or and reflection coefficient as well as solute to effective pore size ratio – control the access of such micropollutants to the inner surface, pore size, porosity and thickness as well as morphology or shape of inner voids determines the available area for sorption. The interaction mechanisms are governed, most likely, by hydrophobic as well as solvation effects and interplay of molecular and supramolecular interactions such as hydrogen bonding, π-cation/anion interactions, π-π stacking, ion-dipole and dipole-dipole interactions, the extent of which is naturally dependent on micropollutant and polymer characteristics. Systematic investigations are required to identify and quantify both relative contributions and strength of such interactions and develop suitable surface characterisation tools. This is a difficult endeavour given the complexity of systems, the possibility of several interactions taking place simultaneously and the generally weaker forces involved.

Keywords
Sorption, micropollutant, membrane polymer, hydrogen bonding, supramolecular interactions, nanofiltration.

1 Introduction

Micropollutants in water are a rapidly emerging global problem that seriously threatens environmental and human health. This can be attributed to the interference with hormonal functions such as behavioural development and fertility. Micropollutants are natural as well as anthropogenic persistent chemicals, such as pesticides, pharmaceuticals, personal care products, plasticizers, and many other groups such as antibiotics, hormones and endocrine disrupters. Many micropollutants accumulate in the environment due to their persistence and increasingly occur in water at measurable concentrations [1-3]. There has been much debate on the health effect of micropollutants such as the disrupting effect on the endocrine system [3-6]. Although proof of adverse effects on mammals from water sources is still being established, due to increasing regulations and for precautionary reasons the removal of those pollutants has become a priority.

Many contaminants originate from wastewater effluents where relatively high concentrations (μg/L) such as pharmaceuticals and antidepressants have been measured. This evidences an incomplete removal by conventional treatment processes [7-16]. While synthetic steroid hormones (such as contraceptive pill, menopause or chemotherapy drugs) generally only occur at trace level concentrations in wastewater effluents, in US streams concentrations of steroid hormones of more than 100 ng/L [12] and up to μg/L for pharmaceuticals, anti-depressants and hormones were measured [17]. This was attributed to effluent discharge. Wells in the vicinity of a WWTP have higher concentrations of pharmaceuticals (up to 300 ng/L) compared to other upstream wells (<50 ng/L) [15]. In a UK survey on two rivers an increase in estrone concentration was measured due to the discharge of sewage treatment works [11]. In one of the rivers the estrone concentration profile downstream clearly followed the profile of estrone concentration of the plant effluent. Further, estrogens have also been found in sediments on the ocean floor surrounding sewage outfalls [18].

Micropollutants are an increasing health threat due to the accumulation of persistent organic pollutants in the environment. The increasing abundance of a vast range of pollutants in waterways is causing concern of exposure from drinking water. In consequence, advanced treatment technologies are required to effectively eliminate such micropollutants. Activated carbon adsorption and coagulation are generally less effective due to the low concentrations of micropollutants and competitive sorption between natural organic matter and micropollutants [19, 20]. Other alternatives are advanced oxidation, although those processes produce an array of unknown by-products with an often equal or higher toxicity [1, 21, 22]. Membrane technology is used predominantly for micropollutant control in water and wastewater treatment as well as in water reuse applications. Nanofiltration (NF) and reverse osmosis (RO) are the most suitable membrane processes for micropollutant control while more porous processes such as microfiltration (MF) and ultrafiltration (UF) cannot retain such small molecules. However, NF and RO removal of micropollutants is reported as erratic and not predictable from molecular weight of micropollutants [23-39].

In the last decade micropollutant breakthrough curves have been reported in the NF literature [23-25]. The important role of micropollutant sorption to polymeric materials used in water treatment has become apparent. This paper provides a state-of-the art review of the mechanisms and parameters responsible for micropollutant retention and sorption to membrane polymers in water treatment applications. Limitations of current knowledge and potential new approaches to find such interaction mechanisms are outlined. Better understanding of these interactions will enable the reduction of adsorption onto polymeric membranes if it is an unwanted

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mechanism that alters removal efficiency. Alternatively, new water treatment processes may result that take advantage of such sorption mechanisms for enhanced removal of micropollutants. For example, polymeric materials that are highly effective in adsorption can be used as novel membrane materials. Such novel materials may incorporate specific selectivity for target micropollutants.

While the mechanisms described in this paper apply to most micropollutants to varying degrees, depending on chemical characteristics of micropollutants, the group of estrogens was selected for this review to allow a better focus on sorption mechanisms.

2 Micropollutant Characteristics: the Group of Estrogens

The molecular structure and other characteristics of estrogens are summarised in Table 1. While to date no correlation between a single micropollutant characteristic and membrane retention and sorption could be identified, the characteristics contribute to various interaction mechanisms. Estrone, estradiol and estriol are natural estrogens which are derived from cholesterol and commonly found in excreta of humans and animals. Testosterone and progesterone, also manufactured by a mammal body are steroid hormones. There are several non-steroidal chemicals synthetically manufactured which can interact with estrogen receptors such as ethinylestradiol, mestranol, diethylstilbestrol. Endocrine disrupting chemicals (EDCs, also referred to as hormonally active agents), are substances that disrupt the physiological function of endogenous hormones by acting like hormones in the endocrine system [26]. Examples of EDCs are contraceptive pill compounds, plasticizers, pesticides, and many other chemicals.

[Table 1]

Chemical characteristics ultimately determine treatability and sorption of micropollutants. A major difficulty in removing such micropollutants from water is not only the small concentration in which they occur and are physiologically active, but also their small size or molecular weight (MW). The MW of the hormones is very similar, varying between 268 and 315 g/mol. According to their MW these compounds are expected to be retained by NF and RO while they are too small for retention by MF and UF.

The pK_a shows the acid dissociation constant at which the hormones lose a hydrogen atom and become negatively charged. The hormones that have a phenolic hydroxyl group all dissociate in the same pH range; between 10.2 and 10.5. At the pH above the pK_a, charge repulsion between the negatively charged hormone and the negatively charged membrane is expected to occur.

The Log K_{OW} parameter measures the hydrophobicity of the hormones by partitioning between octanol and water. As a general rule of thumb, compounds with Log K_{OW} >2.5 are expected to accumulate in solid phases instead of being soluble in the aqueous phase. The Log K_{OW} values for the hormones described in Table 1 are above 2.5 (up to 5.1). Therefore hormones are expected to interact with the membranes by hydrophobic interactions [27, 28].

Estrogen solubility in water is reasonably low (0.3 to 441 mg/L) with significant variability in published data. Dipole moments give an indication on the polarity of the molecules and vary from 1.6 to 4.6 Debye. The molecules with larger difference between positive and negative electrical charges have a higher dipole moment values [29]. Dipole moments of the molecules are important considering that considerable attractive interactions may occur because of the alignment of one dipole molecule with another [30].

Other characteristics considered have been molecular shape and size [31-34]. Van der Bruggen *et al.* [31] showed that molecular weight (MW) is a good indicator of NF and RO retention compared to other molecular sizes such as Stokes diameter. In general, the bigger the molecular size, the higher the retention [31-33]. Kiso *et al.* [35] obtained a clear increase of retention with increase of molecular size (such as molecular width, molecular mean size, and molecular weight) for alcohols and saccharides. However in a later study [36] this clear trend with molecular width

was only obtained for one of the NF membranes used and not for the other 3 membranes. Molecular shape can be exploited to prepare molecular imprints in polymers to create specific sorption characteristics.

Proton donor and acceptor characteristics are further characteristics that may affect interaction with polymers, in particular the ability to form hydrogen bonds. H-bonding has been attributed to play a predominant factor in the transport of estrogens in biological systems [37-42]. The hormones such as E1, E2 and DES all possess a phenol group which is electron-rich [43] and can therefore have the potential to form π-π bonding with electron deficient phenyl groups [30] of the polymers.

Such micropollutant characteristics affect the retention and sorption by membranes and this will be examined in the following sections.

3 Retention of Micropollutants by Polymeric Membranes

The retention of micropollutants such as estrogens varies significantly with membrane process type, membrane characteristics, operating conditions, specific micropollutant characteristics and membrane fouling. In MF and UF micropollutants such as estrogens are not usually retained due to the small molecular weight. However, retention can be increased through association of micropollutants with retained matter or hybrid processes such as powdered activated carbon coupled with MF or UF [44-46].

In NF and RO retention of estrogens can vary from 0 to near 100% depending on the membrane (see Figure 1). Such variation invites a thorough investigation of retention mechanisms to achieve a more reliable and predictable performance.

[Figure 1]

Both size and charge are important and the mechanisms of micropollutant removal can be summarised as illustrated in Figure 2. Any non-retained micropollutants will penetrate into the polymer matrix, while those retained are accumulating in the boundary layer (membrane surface).

Steric Exclusion is a first mechanism that is essentially a sieving principle (Figure 2A) determined by micropollutant size. Pollutants larger than the membrane pore size are normally retained because of a sieving effect which is traditionally more obvious for larger pore sizes and particles [17, 24, 31, 47-53]. While this mechanism is thought to be well established in membrane filtration, unexpected results have been observed with retention of some micropollutants considerably lower than expected based on molecular weight [34, 54]. Some have attributed such variation to molecular length and shape [37, 55, 56] although Van der Bruggen *et al.* [31] concluded that correlation of retention with size parameters other than MW (*e.g.* Stokes diameter) was only a marginal improvement.

[Figure 2]

Charge and *Donnan exclusion* are further mechanisms of exclusion of solutes by membranes. Those describe the repulsion between a charged solute and a charged membrane (Figure 2B). Naturally, this process is well understood for inorganic salts, while organic acids, macromolecules and micropollutant behaviour needs to be better understood. Micropollutants of similar or smaller size than the membrane pores can be retained due to charge repulsion between the membrane polymer and the micropollutant [23, 24, 31, 53, 57-62]. This mechanism is applicable for charged micropollutants only and hence speciation is very important. Speciation is micropollutant specific and can change depending on water characteristics as well as solute-solute interactions that result in ligand formation and complexation. Most estrogens that have a phenolic hydroxyl (OH) group dissociate above pH 10.25 to 10.5. In consequence those estrogens are uncharged at neutral

pH while charge interactions occur above pH 10. Retention of estrone has been shown to increase at pH>10 due to the dissociation of the hormone [57, 63].

The charge of membrane polymers can be measured using streaming potential methods and is generally negative at neutral to high pH for common NF and RO membranes [41, 59, 63-65]. Such charge results from chemical modification of polymer surfaces. Actual charge depends on membrane polymer characteristics, functional group content as well as solution chemistry such as pH, ionic strength and attachment of ions. The increase of ionic strength, for example, decreases retention of charged solutes due to charge shielding between the membrane and the contaminant (*i.e.* Donnan exclusion mechanism) [60, 66-68]. Nghiem *et al.* [60] showed that the addition of calcium ions decreased retention of charged pharmaceuticals even more dramatically than an increase in NaCl concentration. This can be attributed to a more effective charge shielding by calcium ions due to its divalent charge compared to monovalent sodium ions.

To measure estradiol retention by NF as a function of pH, crossflow experiments were conducted. A stainless steel system with a 2.5 L feed tank with a cooling jacket of 0.09 m^2 and a high pressure pump (P200 from Hydra-Cell, UK) was connected to a flat sheet membrane cell (MMS, Switzerland). Temperature was monitored in the retentate by a temperature indicator (WTM Pt 100-0-6 from Condustrie-Metag, Germany). The cooling jacket is connected to a temperature controlled bath (WK 700, Lauda). A back pressure regulator from (KPB1N0A415P60000, Swagelok, UK) allows the pressurization of the system up to 130 bar. The pressure is monitored in both feed and retentate side of the membrane cell with two pressure transducers (S model, Swagelok). The membrane cell hosts a membrane of 46 cm^2 with a flow channel width of 2.5 cm, length of 19.1 cm and height of 0.1 cm. A flow meter was inserted between the pump and the membrane cell to allow for the control of the flow rate (M2SSPI from Hydrasun, UK). Datalogging was set-up (DAQ 55 Omega, UK) allowing for the control of membrane cell inlet and outlet pressure, feed flow rate and temperature. All cross-flow experiments were carried out with an initial feed solution of 100 ng/L of ^{3}H-Estradiol (GE Amersham, UK), feed flow rate of 0.5 or 2 L/min (Reynolds number of 740 and 2800, respectively), 11 bar, 24°C until the membrane was saturated and steady state was reached. For experiments at pH 11, the pH was adjusted with 1 M NaOH (Fisher Scientific, UK).

Higher retention at pH 11 compared to pH 7 is illustrated in Figure 3B where at high pH charge repulsion occurs between the dissociated estradiol and the negatively charged membrane. Retention at pH 11 stabilises at 85%, while at pH 7 retention is only 60% (Figure 3B). However, concentration in the feed decreases gradually, while the permeate concentration increases until equilibrium is reached (Figure 3A). In addition, the retention of micropollutants in NF has been observed to change with time, which is not expected if size and charge are predominant retention mechanisms. The permeate concentration shows a breakthrough curve which evidences that this unsteady trend of concentrations is caused by adsorption of estradiol onto the NF membrane.

[Figure 3]

Adsorption (Figure 2C) and subsequent *sorption diffusion* (Figure 2D) has indeed been confirmed for micropollutants by various polymeric membranes [23, 25-28, 30, 32-34, 36, 40, 56, 68, 78-83]. Nghiem and Schäfer [25] have measured such a breakthrough curve for estrogens at 100 ng/L using a technique with radiolabelled micropollutants. Adsorption however can be affected by solution chemistry. As shown in Figure 3, adsorption is lower at high pH due to charge repulsion (Figure 3C). This is clearly reflected in an increased estradiol mass flux at pH 7 (Figure 3D). The same trends were obtained by Hu *et al*. [63] and McCallum *et al*. [57]. The observation reflects that of a breakthrough curve that is commonly observed in adsorption or ion exchange processes. Notably such adsorption is higher when the retention is lower (Figure 3C), indicating that penetration of micropollutants into the polymer matrix enhances sorption, while sorption itself may also decrease retention.

Solute-solute interactions and *fouling* can make the determination of actual retention mechanisms difficult and adsorption in particular is often confused with *membrane deposit formation* or *concentration polarization* phenomena. During filtration the deposits of retained materials as well as fouling change the membrane surface and hence possible charge, steric and sorption interactions. In addition, changes in retention over time or in different water matrices may occur due to solute-solute interactions (Figure 2E) as well as micropollutant-fouling layer interactions (Figure 2F). Such phenomena can, for example, induce micropollutant retention by ultrafiltration membranes [45, 46, 69] or cause desorption of adsorbed micropollutants making retention mechanisms in real waters a very complex affair.

Given that adsorption is a very common observation in membrane filtration of micropollutants this mechanism will be investigated systematically in this review to gain a better understanding. In the following section transport models will be summarised before returning to adsorption in more mechanistic detail.

4 Micropollutant Transport Models for Membrane Filtration

Descriptions of solute transport in RO membranes were originally given by the *irreversible thermodynamic model* [70, 71]. The membrane was treated like a black box, no membrane structural or electrical parameters were acquired and scarce information about the transport mechanisms inside the membrane could be obtained [72].

The *solution-diffusion model* was proposed where it considers that each permeant dissolves in the membrane and is transported by diffusion due to its gradient in chemical potential through a non-porous membrane [72]. The solute flux is independent of permeation pressure while the solvent flux increases proportionally to it. Retention must therefore increase with pressure. This was confirmed for metals, some ions and saccharides, namely uranium, raffinose, sodium, magnesium and calcium [66, 68, 73, 74].

For NF membranes, there is some debate about the existence of discrete pores. In this case the solution-diffusion model is incomplete and a convection term should be included that takes account of solute transport through membrane pores. The retention of uncharged solutes in NF membranes can be described with the *hydrodynamic model* [75] previously described. The transport takes into account diffusion and hindered convection, caused by the difference between solute size and pore size. For charged solutes such as ions or organic acids, the addition of the membrane and ion electrochemical potential derives in the *extended Nernst-Planck equation* [73]. This last model not only allows determining the same parameters as the hydrodynamic model but also allows the determination of the effective membrane charge density [54, 76, 77].

Generally, both the solution diffusion model and the hydrodynamic model describe an increase of retention for solutes with pressure. However, for some micropollutants the opposite trend is observed, *e.g.* with hormones [50, 78], pesticides [53, 61], volatile organic carbon (VOC such as chloroform) [47], endocrine disrupting chemicals (EDCs) such as nonylphenol (NP) [79] and pharmaceuticals [61] where retention decreases with pressure. It is thought that the interaction of micropollutants with the membrane polymer plays an important role [54] and contributes to the reduced retention at higher pressure. However this phenomenon is not directly linked with the ratio between the solute and pore radius ($\lambda=R_{solute}/R_{pore}$). It could be argued that for $\lambda<1$, the solutes can penetrate the membrane and be less retained. However, for nanofiltration of Na_2SO_4, glycerine and glucose as examples of non-adsorbing compounds with $\lambda<1$, retention increases with increase of pressure [73, 80]. This trend is not always verified for micropollutants with $\lambda<1$ [78]. When pores physically exist the issue of steric hindrance or size exclusion is obvious. However, considering a pure steric hindrance model is not accurate in the case of dense materials and adsorbing solutes [54]. Solute retention depends not only on solute size but also on adsorption and chemical organic characteristics such as hydrophobicity, as well as convection and diffusion mechanisms [81].

Adsorption of micropollutants to the membrane polymer is usually not taken into account in micropollutant retention models [54, 58, 59, 82]. In consequence, retention, permeate

concentration and mass flux are therefore often wrongly determined. Retention, in particular, is commonly overestimated when based on size. The interaction that exists between adsorbing micropollutants and the membrane was incorporated in the hydrodynamic model for NF using an affinity concept [83]. Although retention was predicted well and increased with permeate flux for the adsorbing contaminants, for other contaminants, retention decreased with increase of flux [78]. Furthermore, a simplified approach to model the retention of several micropollutants in NF has been developed [82]. For some micropollutants, such as xeno-estrogens, high membrane adsorption occurred and in consequence no permeate concentration was measurable. This prevents the application of this model, which does not take adsorption into account, for solutes that interact with membranes. For other solutes, diffusion only transport closely matched the measured retention. In another study the irreversible thermodynamic model was used as a basis to understand if convection or diffusion were the predominant contributor in the solute (DBP and halogenated solvents) permeate flux for NF and RO membranes [84]. This proved problematic for adsorbing compounds and the membranes had to be presaturated to achieve steady state. When reaching steady state proved to be impossible as for the case of trichloroethene, no conclusions could be drawn.

Interestingly, adsorption has been considered in a modified sorption-diffusion model for RO that added adsorption induced flux decline to pressure [85]. Results confirm flux decline due to the adsorption of the organic compounds on the membrane polymer through specific adsorption (*e.g.* hydrogen bonding). Organics may compete with water for adsorption sites and decreasing water content on the membrane and flux. Further, this model described the transient permeate concentration behaviour more adequately that the previous model which considered steady state conditions of water and solute flux across the membrane, by assuming adsorption-diffusion transport of organics in the membrane polymer. Shortfalls of this model remain (i) the inapplicability to NF due to a missing convection element, and (ii) the common absence of a flux reduction element due to micropollutant sorption [85, 86]. This outlines the need for retention models that are solute – and no doubt concentration - specific and consider possible solute-membrane interactions. Some attempts have been made in this direction using artificial neural networks. The principal component analysis method (quantitative structure relations or QSR) has been developed to obtain a model that describes retention as a function of the contaminants most important variables (*e.g.* molecular width and depth) by nanofiltration membranes [55, 56] and the NF membrane characteristics such as roughness or active layer thickness [32]. Limitations of such models are the validity for certain boundary conditions only, and while simple in nature, they cannot replace the understanding of fundamental mechanisms.

A further complexity that is not yet theoretically predictable is the behaviour of micropollutant mixtures. In real waters many micropollutants are found together with other organics such as effluent or natural organic matter. This can result in solute-solute interactions [87]. When organic matter is present in solution enhanced retention is generally obtained for micropollutants [45, 52, 58, 61, 78, 88-91] due to partitioning of the micropollutants into the retained organics [92, 93]. Higher adsorption is obtained, possibly on both membrane and organic matter layer that is formed on the membrane surface [62, 63, 88, 89, 94]. According to some studies, the presence of a humic acid fouling layer renders the membrane more hydrophobic, enhancing estrone adsorption [63, 89]. However, this increased sorption may be attributable to interactions between humic acid and micropollutants more so than increased hydrophobicity. In contrast, a decrease in micropollutant adsorption may occur when natural organics and micropollutants compete for sorption sites [57, 92, 95-99]. Competition for sorption sites occurs often between micropollutants or between micropollutants and other organics at much higher concentrations. In single solution the sorption is higher than in mixtures and retention lower. Competition decreases the retention when compared to a single micropollutant solution [92, 100], while retention of these adsorbing compounds is enhanced when their adsorption is decreased [86]. This shows the close relationship between adsorption phenomena and retention of micropollutants. Several models to predict the amount adsorbed on a membrane for mixtures based on the amount adsorbed with only one compound has also been developed [101].

While solute retention in NF and RO is reasonably well understood, the retention of adsorbing micropollutants cannot currently be adequately described. Results obtained with pristine and saturated membranes often show diametrically opposed results making the interpretation of literature difficult. Understanding of adsorption mechanisms and transient adsorption will be instrumental to fully incorporate adsorption phenomena into membrane models successfully. In consequence this adsorption will be investigated below.

5 Micropollutant Sorption in Membrane Filtration

Sorption by membrane polymers occurs across the range of available processes and polymers. In this section a number of examples are provided from pressure driven membrane processes and electrodialysis. Observation of micropollutant sorption to membrane polymers is a recent phenomenon. This is presumably due to the development of analytical techniques that facilitate the detection of molecules in nanogram quantities of pollutants of very low concentration. However, such sorption would be a very common occurrence for many pollutants albeit often not measurable. Sorption of organics is well recognised as a conditioning film for subsequent biofilm attachment. Micropollutants accumulate in biofilms. However, the understanding of the impact of estrogens on growth of such biofilms or their degradation by biofilms is not yet established [102, 103].

While porous membranes such as MF and UF do not retain micropollutants, the polymer surface may adsorb significant amounts. This has resulted in the removal of estrone by a 0.2 µm MF polypropylene membrane of more than 95% [104] which can only be attributed to adsorption. Other examples showed >34% of 17β estradiol adsorption on a ultrathin polyimide UF membrane [105] whereas 36% and 30% retention of bisphenol A was observed in other studies [46, 106]. UF membranes were used to recover 6α-methylprednisolone from cell suspensions, and 27% and 31% of hormone was adsorbed on two different MWCO UF polysulphone membranes [107]. Jermann *et al*. [69] have shown low estradiol retention by a hydrophilic UF membrane, while a hydrophobic membrane showed very high retention with a gradual decrease as the polymer saturated with estradiol. Higher retention was attributed to organic matter fouling while Neale and Schäfer quantified the contribution of organic matter – micropollutant interactions in the absence of significant sorption for a hydrophilic membrane [108]. This illustrates the complexity of such interactions.

Naturally, the majority of micropollutant sorption results have been published in NF, while comparison can be very interesting. High adsorption of the hormones estradiol, progesterone and testosterone on both a UF (sulphonated polyethersulphone coated with polyimide) and NF (polyamide) membranes was observed, while surprisingly estrone did not adsorb [96]. Adsorption of estradiol was lower for NF than UF; for a delivered mass of estradiol of 1 µg/cm^2, the UF membrane adsorbed about 0.5 µg/cm^2 and the NF adsorbed about 0.2 µg/cm^2 [95]. Adsorption occurs on different membrane layers and alters if static adsorption (no pressure/filtration) as compared to filtration conditions. For example, adsorption of several hormones to NF200 polyamide membrane was studied in a stirred cell system without pressure. Adsorption of all hormones varied between 0.20 and 0.35 ng/cm^2 for a feed concentration of 10 µg/L [52]. Adsorption of 100 ng/L estrone to two NF membranes made of cellulose acetate (CK, MWCO 560 g/mol) and polyamide (DL, MWCO 490 g/mol) resulted in a decrease in feed concentration due to sorption of 20% and 65%, respectively. According to McCallum *et al.* [57] adsorption of estradiol occurred mainly in the polysulphone layer compared to the polyamide layer, where samples of different stages of membrane manufacturing were used. However the layers used in this study were provided from the manufacturing process of a different membrane (NE 70 instead of NF 270). Williams *et al.* [85] on the other hand obtained higher adsorption of organic pollutants such as benzene and 2-chlorophenol on the polyamide layer when compared to the polysulphone layer showing that interactions are micropollutant and membrane material specific.

Charge repulsion reduces adsorption (see Figure 3C) and this is confirmed in Figure 4 for a number of different membranes. A stirred-cell was used for experiments at 5 bar, a feed concentration of 100 ng/L of estrone (E1) and estradiol (E2), and 1 mM $NaHCO_3$ and 20 mM NaCl for the TFC-S and TFC-SR2 membranes [109, 110]. The X20 experiment was carried out at 10 bar [25]. Hu *et al.* [63] used a cross-flow system with 1mM $NaHCO_3$, 8mM NaCl, 14 bar, 100 ng/L estradiol with the DL membrane until the membrane was saturated. Retention varies depending on membrane type and while this is consistent from pH 3 to 10, above pH 10 both retention and adsorption decrease drastically for all membranes except the DL membrane. This change can be attributed to the fact that these membranes were not at equilibrium and in consequence, the retention measured is misleading. In the presence of synthetic urine, ethinylestradiol adsorbed to the NF270 membrane in the order of 3.6 µg/cm^2 for a very high feed concentration of 3 mg/L (10 µM) and an effective membrane area of 0.0028 m^2 [93]. High adsorption of several hormones in batch experiments in the following increasing order of adsorption were measured: X20 (*MWCO <200 Da, polyamide*) > TS80 (*MWCO <200 Da, polyamide*) > NF270 (*MWCO 400 Da, polyamide*) > UE10 (*MWCO 10000 Da, polysulphone*) [111]. MWCO and material effects cannot be distinguished.

[Figure 4]

Adsorption is lowest for the membrane with highest retention (X20) indicating that 'pore size' may play an important role in adsorption. In order to investigate the relationship between such 'pore size' and adsorption, a number of membranes were characterised in terms of molecular weight cut off (MWCO) and pore radius. The pore radius and the ratio membrane active layer thickness/porosity was determined for each membrane using the hydrodynamic model [75, 76] with neutral solutes (methanol, dioxane, xylose and dextrose). This model assumes perfect cylindrical pores of identical pore radius, solutes of spherical shape and that retention of the solutes only occurs through steric exclusion. The mentioned parameters are obtained by curve fitting the hydrodynamic model to the real solute retention variation with permeate flux. The same methodology described by Nghiem *et al.* [54] was adopted for the BW30, NF90 and NF270 characterisation using a cross-flow system. The TFC-SR2 and TFC-SR3 characteristics were determined with the same method in stirred-cells [112]. The active surface area (membrane surface area including pore surface area) was estimated with an average of active layer thickness of the membranes from literature [113-117] and summarised in Table 2. With the membrane active layer thickness, porosity can be obtained and therefore the internal surface area of the membrane active layers can be calculated. Since no active layer thickness has been published for the TFC-SR3 membrane an average value of reported thicknesses for the TFC-S and TFC-SR2 membranes was determined [113, 118-120].

[Table 2]

The equivalent sphere radius of estradiol was calculated with the Stokes-Einstein equation. Crossflow experiments were carried out with the same system as described for Figure 3. Retention of estradiol decreased with increasing pore radius above the estimated radius of estradiol of 0.4 nm from about 80% to 30%. Mass adsorbed increased with pore radius for both the membrane area (as per sheet size) as well as per estimated total membrane area available to sorption. Sorption is lower when regarded as per available internal surface area suggesting that adsorption occurs internally and increases with increasing available area. It should be noted here that this area only considers the internal area of the active layer (polyamide) and not the polysulphone supporting layer. More work is required to differentiate between those materials systematically.

[Figure 5]

Sorption to membrane polymers is not unique to NF and RO. In fact, sorption to electrodialysis (ED) membranes can be significantly higher than for other membranes. Pronk *et al.*

[121] used polyethersulphone electrodialysis membranes with an effective surface area of 49 cm^2 per sheet in an ED stack of two cell pairs to recover salts from urine containing ethinylestradiol (EE2). The result showed that approximately 230 µmole of EE2 was adsorbed on the membrane when 400 µmole of the hormone is added in initial urine solution at a high concentration of 10 µM (about 3 mg/L) [121]. Taking into account the molecular weight of ethinylestradiol the adsorption was estimated as 139 µg EE2/cm^2 where the initial EE2 mass added into solution was as high as 119 mg. Banasiak [122] has measured the adsorption of different hormones to electrodialysis membranes (see Figure 6) at a concentration of 100 ng/L. The experiments showed an adsorption as high as 1.2 ng/cm^2.

[Figure 6]

Such enhanced adsorption can be attributed to very thick membranes in ED as compared to an active layer thickness in NF or RO. In addition, the effective area is very high due to the internal porosity observed in ED. Electrodialysis membranes can be classified in three groups regarding their size of clusters in swollen state. These groups are homogeneous, microheterogeneous and heterogeneous. The 'pore size' of homogenous Nafion ED membranes is about 1 nm whereas Nafion 117 has a pore diameter of about 6 nm [123]. Eurodia/Neosepta electrodialysis membranes have a very low molecular weight cut off (350 Da MWCO) [124]. Khulbe *et al.*, states that dialysis membranes have a pore diameter changing between 2 and 5 nm [125]. In contrast, several hollow fibre electrodialysis membranes were imaged by AFM and TEM and the results showed that pore diameter at the inner surface was 10.5 nm and 12.9 nm for polyester-polymer alloy (PEPA) and polysulphone polyvinylpirrolidone (PS+PVP) materials, respectively [126]. This indicates a nanoporous structure throughout the membrane with a thickness of hundreds of µm, which illustrated the role such an internal area plays for micropollutant adsorption- or absorption.

6 Micropollutant Sorption by active Polymer Surface Area

The mechanisms of micropollutant sorption to membrane polymers is to date not well understood. Steinle-Darling *et al.* [127] described two mechanisms of micropollutant sorption; a first one being *adsorption* to the membrane surface, and a second being internal *absorption* into the membrane pore structure. Solvation in the membrane and diffusion within are processes that lead from adsorption to absorption. While this process is conceptually reasonable, the reality in various membrane processes may be more complex. In porous membranes, for example, the available membrane surface area will extend into the material and it becomes debatable where adsorption ends and absorption starts. A further complication is the material characteristics of composite membranes that consist of support layers and active layers of different material, thickness, pore size and porosity. This will alter the available surface area considerably even without considering the heterogeneity of such materials. It is difficult, if not impossible, to determine the internal polymer surface area available for micropollutant sorption.

To investigate this effect of surface area systematically, adsorption of estrone (E1) to polystyrene nanoparticles separated by UF membranes was investigated (see Figure 7). Regenerated cellulose ultrafiltration (UF) membranes with a polypropylene support layer of 1, 3, 5 kDa MWCO supplied by Millipore (Bedford, US) were used. Those membranes were chosen as sorption is minimal and fouling does not occur at those small MWCOs [128-130] for the chosen nanoparticles during the given experiments. Polystyrene nanoparticles with a size range of 46 nm to 3 µm were purchased from Polysciences, Inc. (Eppelheim, Germany). The experiments were conducted with stainless steel stirred cells in which solution operated at 300 rpm with a magnetic stirrer. Radiolabelled [2,4,6,7-^{3}H] estrone (2.45 TBq/mmol) with a radioactive concentration of 37 MBq/mL was purchased from Perkin Elmer (Beaconsfield, UK). Prior to the experiments, the membranes were compacted for 30 minutes and pure water flux determined. 15.7 mg/L of

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nanoparticles were added in 100 mL pure water solution and deposited on the surface of the membrane by filtering the solution through the membrane at 5 bar. Afterwards, 450 mL of stock solution was filtered by collecting 8 samples of 50 mL permeate samples until 50 mL of concentrate remained in the stirred cell.

[Figure 7]

Results indicate that adsorption of estrone (E1) decreases sharply with increase of particle size due to the reduced surface area of larger particles. Surface normalised sorption increases with particle size which indicates that the available surface is not saturated. Increased sorption with the lower MWCO membranes can be attributed to a longer contact time between micropollutants and the retained nanoparticles due to the lower flux. Clearly, sorption can be attributed to surface area when such a surface area can be calculated accurately which is the case for such spherical nanoparticles. Sorption is directly related to the available surface area and this has direct implications to sorption of membrane polymers. However, for generally very heterogeneous polymers, the determination of the actual surface area of a membrane polymer is very difficult if not impossible to determine accurately.

To evaluate such surface variability, the internal membrane surface area has been estimated as a function of pore size of cylindrical pores (Figure 8A-C) and voids between spherical grains (Figure 8D) with varying thickness and porosity. A membrane surface area of 100 cm^2 was considered and equation (1) was used for perfectly shaped cylindrical pores to determine surface area from pore size, porosity and active layer thickness.

$$\text{Total Area} = \text{Surface Area} + \text{Internal Area} = WL(1-\varepsilon) + \frac{2LW\varepsilon\delta}{r_p} \qquad (1)$$

Where W and L are the membrane width and length (10 cm) respectively, ε is the membrane porosity, δ is the active layer thickness and r_p is the pore radius.

For membranes made from spherical grains which is the case for some MF, UF and ED membranes, a cubic close packing of spherical grains was used and equation (2) shows the relationship between the surface area, active layer thickness and sphere radius.

$$Surface\ Area = \frac{16WL\delta\pi r_{sphere}^{\ 2}}{(2\sqrt{2r_{sphere}})^3} \qquad (2)$$

Where r_{sphere} is the sphere radius. This indicates a rapid increase of internally available surface area with decreasing pore size at similar porosity and a linear increase of this surface area with membrane thickness.

[Figure 8]

While such calculations can be carried out for conceptual or ideal membrane characteristics, the characterisation of pore size, membrane thickness and porosity (and in consequence internal pore area) of real membranes, in particular composite membranes used for NF is very difficult, if possible at all.

A range of characterisation tools exists for membrane characteristics such as porosity, pore size and active layer thickness. Active layer thickness can be measured by SEM [115, 131, 132], Rutherford Backscattering Spectrometry [131], TEM [133], as well as Impedance Spectroscopy [134]. Thickness of the active layer has been determined by Freger *et al.* [114, 133, 135] to be in the order of 10-200 nm for NF and 200-350 nm for RO membranes of polyamide active layer. Uranyl nitrate staining of the active layer followed by transmission electron microscopy was used. The work illustrated how highly non-uniform polymer density and charged surface groups are

distributed across the active polyamide layer. The densest part of the layer may be covered by an extensive surface roughness which makes the accurate determination of surface available for sorption extremely difficult. Surface roughness for three thin film composite NF membranes – with polyamide active layers - is shown in Figure 9. This image implies a very high surface roughness for TFC membranes.

Membrane surface roughness can be quantified by AFM [136-138]. Values for average roughness between 0.4 and 5 nm were reported, while some membranes show much higher values, 28 nm for NF90 [139] and >60 nm for BW30 [140]. Surface roughness for cellulose acetate membrane supports have been reported as high as 17 nm [138]. Using such values AFM can be used to estimate the surface area of membranes, where for a projection area of 100 μm^2 surface areas between 150 and 180 μm^2 were reported for an average surface roughness between 40 and 85 nm [141]. It is possible that such figures are an underestimate when the internal membrane structure is considered accurately, the likely range of which is evident from Figure 8. Ultimately such values will remain averages that are prone to be biased to properties visible from the surface of the membrane while properties within the material remain unknown.

[Figure 9]

Positron annihilation spectroscopy (PAS) can be used to determine the top layer porosity [115]. A difference between the pore size of the top layer and support layer can be obtained indirectly, although no physical value of porosity was published. An evident increase in porosity is observed at the transition between the active layer to the more porous sub-layer. Porosity can however be determined experimentally. Several authors have used the hydrodynamic model [75] by filtrating neutral organic and inorganic solutes to obtain the pore radius, active layer thickness to porosity ratio [54, 76, 77, 142]. With the knowledge of the thickness of the active layer (*e.g.* by using TEM), one can calculate the active layer porosity. Pore size distribution on the other hand can be used to determine the number of pores and the pore radius of several commercially available membranes [143, 144].

Attempts to identify a discrete pore size of NF membranes by AFM resulted in estimates from 0.1 to 2 nm [139, 145]. While such methods are limited to pores visible from the membrane surface and the existence of discrete pores in nanofiltration is subject to ongoing controversy, the results obtained are in the same order of magnitude as effective pore sizes determined by other methods. As previously mentioned the hydrodynamic model can also be used to determine the membrane pore radius. As an illustration the pore radius obtained for the NF270, TFC-SR2 and NF90 were 0.42, 0.52 and 0.34 nm respectively (Table 2).

In addition to physical parameters of the membrane such as internal surface area and roughness, chemical characteristics of the micropollutant and of membrane polymers alter adsorption behaviour.

7 Micropollutant Sorption by different Polymer Materials

The observation of micropollutant sorption to polymeric materials is not new and early observations were made of interactions with laboratory equipment. For example, Petri dishes (PVC) were found to adsorb significant amounts of hormones and results were verified with grinded PVC [146]. One study established that polystyrene plastic ware adsorbed 38% and 43% of 17β-estradiol and progesterone, respectively [147], while another study reported that the majority of parathyroid hormone sorbed to borosilicate glass tubes, polycarbonate and cellulose nitrate. Sorption to polypropylene tubes was lower and equilibrium was reached within 4 hours [148].

Packaging materials equally have an adsorption capacity for hormones. Results using granular materials found very high adsorption capacities for polystyrol (6 ng/cm²), for glass (18 ng/cm² and 105 ng/cm² depending on the glass type), for polypropylene (60 ng/cm²), for polyethylene (PE, 75 ng/cm²), for Lupolen (low density polyethylene, 180 ng/cm²) and for Cellidor

(Celluloseacetobutyrat; more than 420 ng/cm²) [149]. While concentration values were not provided the high adsorption most likely indicates a relatively high concentration of contaminants used.

Such observations are not unique to hormones. Volatile chemicals (trichloroethene and tetrachloroethene) to polyethylene (PE) was competitive for hydrophobic micropore spaces in the polymer. Such competition is anticipated when solutes of similar polarity and size compete for a limited number of sites, and smaller micropore spaces dominate sorption interactions [150]. Adsorption of hydrophobic chemicals, PCBs, DDE and NP (nonlyphenol) to polypropylene (PP) marine resin pellets collected from the Japanese coast was reported to vary from 4-117 ng/g, 0.16-3.1 ng/g, 0.13-16 µg/g for PCB, DDE and NP, respectively. Determination of the specific surface area of PP pellets was estimated as 25cm^2/g and surface specific adsorption results were 4.7 ng/cm^2, 0.12 ng/cm^2, 0.36 µg/cm^2 for PCB, DDE and NP, respectively [151]. Significant sorption of hydrophobic endocrine disrupting compounds to porous polysulphone beads was reported [152].

Sorption has also been observed for filters used in sample preparation resulting in significant losses of analytes. Different types of filter materials were tested for estradiol adsorption and the results showed that cellulose acetate and cellulose nitrate adsorbed the most estradiol compared to glass fibre and paper materials [149]. Adsorption of up to 50% of feed estradiol concentration on a cellulose acetate filter was observed [153].

Sorption interactions are exploited for analytical purposes which is commonly the case in chromatography as well as sample preparation. Solid phase extraction (SPE) is used for the concentration of analytes in samples. The most widely used SPE sorbents for micropollutants are alkyl-bonded silicas (C18 silica, C2 silica), copolymer sorbents such as cross-linked polystyrene divinylbenzene, and hydrophilic lipophilic balanced polymers. Each has specific contaminant applications [154, 155]. C18 resins and other polymeric sorbents have been used in several studies separate or in combination for purification and determination of pesticides, estrogens and progestogens with SPE [156-158]. Solid phase micro-extraction (SPME) sorbs a fraction of the analyte and can be used for the quantification of both analyte as well as analyte interactions with other dissolved molecules. Polyacrylate has been used for the detection of estrogens in water and their interactions with organic matter [87, 159]. Polydimethylsiloxane (PDMS), divinylbenzene (DB), polyacrylate (PA), as well as Carboxen (CAR; a carbon molecular sieve) and Carbowax (CW; polyethylene glycol) are other commonly used coating polymers for SPME of organics [160].

Similar sorption phenomena are observed in other water treatment applications that involve polymer interfaces. For example, magnetic ion exchange resin (MIEX) developed for enhanced natural organics removal, sorbs significant amounts of uncharged micropollutants such as estrogens [161]. The resin has a macroporous polyacrylate shell with quaternary ammonium functional groups for ion exchange.

These results highlight an affinity of certain organic solutes for polymeric materials and a strong material dependence on interactions. While it is no surprise that membrane polymers adsorb micropollutants, the mechanisms of micropollutant adsorption onto polymers are to date scarce not well understood and hence a systematic investigation is required. For this reason a range of polymers (see Table 3) commonly used for membrane materials has been selected for preliminary investigation and the very novel results are subsequently presented in this review.

[Table 3]

While differences in sorption are significant for different polymers, a complete lack of understanding exists as to why this is the case. It is a hypothesis that once adsorption facilitates micropollutant diffusion through the polymer matrix even if larger than 'pores'. This is driven to some extent, but not solely, by a concentration gradient and may explain some of the incomplete retention observed at larger scale. This mechanism is poorly understood and hence neither predictable, nor controllable. Other factors that contribute to sorption may be the ability of a micropollutant to interact specifically with polymer functional groups, Gibbs free energy of the localised environment as well as other factors.

Proprietary material modification by membrane manufacturers make this challenging if not impossible and it is hence worthwhile studying such interactions with 'pure' polymer materials. Inconsequence sorption of estradiol (E2) was determined for a range of polymers produced from pure pellets by grinding to a size of <500 mm as well as ground membrane polymers (see Figure 10). Figure 10A and B present mass of estradiol adsorbed per mass of polymer for the different polymers, while in Figure 10C and D the results are normalised for the particle size as measured by electron microscopy and analysed with ImageJ version 1.40 assuming that particles have a spherical shape. Polymers used were polyamide (PA; 500µm), polypropylene (PP; 500µm), polysulphone (PSu; 500µm), polyethylene naphthalate (PEN; 500µm), polystyrene (PS; 500µm), polyethylene terephthalate (PET; 500µm), cellulose (CEL; 15µm), NF 270 (PA active layer, PSu and Polyester support layer, PET; 500µm) and UF (CEL active layer, PP support layer; 500µm), PVDF (500µm), polyethylene high density (HDPE; 500µm), polyethersulphone (PES GF; 500µm), poly(2,6 dimethyl 1,4-phenylene oxide) (PPO; ~5µm), polyethersulphone (PES Radel; 500µm), polysulphone UDEL (PSu U; 500µm) and poly(methyl methacrylate) (PMMA; 36µm).

[Figure 10]

PSu, PP, HDPE, PA, PS, PET, PEN and PES were purchased from Goodfellow (Huntingdon, UK) in the form of 2-3 mm granules. PSu UDEL and PVDF were obtained from Solvay (Brussels, Belgium) in granular form and CEL, PMMA and PPO were purchased from Sigma Aldrich (Gillingham, UK) in powder form. Polymers in granular form were grinded to a size of 0.5 mm with Retsch Ultra Centrifugal Mill ZM 200 (Leeds, UK), in three stages using sieves with 1.00, 0.75 and 0.50 mm openings. Radiolabelled [2,4,6,7-^{3}H] 17β-estradiol (3.15TBq/mmol) from Perkin Elmer (Beaconsfield, UK) was used to prepare 60 mL of 100ng/L solutions. 2.5g of each polymer was added into separate estradiol solutions and the solutions mixed in a Certomat BS-1 UHK-25 shaker (Göttingen, Germany) at 200 rpm and 25ºC. Samples of 1mL were taken with 1 mL syringes at certain time intervals and filtered through 0.7 µm glass microfibre filters (Fisher, Loughborough, UK) which was placed in Millipore Swinnex filter support (Ireland). Based on the results of preliminary experiments where glassfibre filters were chosen due to their lowest sorption of estradiol, after the third sample filtration, the filter reached saturation and the adsorption calculated was due to polymer adsorption. The activity in initial and filtrate samples were counted in triplicate using a Beckman LS 6500 liquid scintillation counter (Fullerton, USA) by mixing 0.5 mL samples with 3.5 mL of Ultima Gold LLT liquid scintillation liquid (Beaconsfield, UK) in 20 mL glass scintillation vials. Experiments were stopped after about 8000 minutes.

Results indicate that sorption of estradiol to polymer particles is a surface phenomenon for polymers with very strong affinities (Figure 10). This is demonstrated from very rapid kinetics as is the case of polyamide (PA). The high sorption to PA is confirmed with a similar result for the NF membrane material (NF270), a thin film composite with a PA active layer. Another highly sorbing polymer is polyethersulphone (PES) although in this case adsorption kinetics are not as quick. Either the phenomenon is not restricted to the polymer surface or due to weaker interactions, the adsorption process is slower. Nonetheless, this study gives a very good indication of the affinity of estradiol to different types of polymers. However given the uncertainties of particle shape and size distribution, it is not possible to distinguish between affinities of polymers that adsorb less. It should be noted that the observed results correlate well with experimental observations to date in NF where active layer consists of PA and presented above. Surprising is the low affinity of polymers that are considered hydrophobic, such as polyvinylidene fluoride (PVDF).

It should be noted here that the polymers used are raw materials. In membrane manufacturing such polymers are processed to have a morphology and porosity. Further, proprietary chemical modifications take place that introduce surface functionality not shown by the primary polymer.

Chemical characteristics, such as the molecular structure and functional groups of the active layer of membranes can be studied with ATR-FTIR [115], while atomic concentration percentages

of C, O, N and S can be obtained by using X-ray photoelectron spectroscopy XPS [134]. Hydrophobicity of polymers is measured as contact angle [162] while for micropollutants hydrophobicity is expressed as octanol water partition coefficient (K_{OW}).

In general the more hydrophobic a compound is, the more it is expected to adsorb onto a surface in contact with water because this requires less free energy compared to forming a "cavity" in the water phase [163]. In the case of membrane polymers higher the hydrophobicity has also been attributed to more adsorption [58, 60, 95, 111, 164]. For example, Boussu *et al.* [164] obtained a clear trend of increasing adsorption with increasing hydrophobicity of the organic compound such as phenylalanine. Two of the more hydrophobic PES membranes adsorbed much higher quantities compared to the phenylalanine membrane. However, some exceptions exist where highly hydrophobic micropollutants adsorbed very little onto NF polyamide or polyethersulphone membranes.

In the specific case of hormones, Dudziak and Bodzek [165] showed that adsorption and retention was not related with hydrophobicity for two different NF membranes (polyamide and cellulose acetate). DES, the most hydrophobic hormone (see Table 1, log K_{OW} 5.07) adsorbed the least for both membranes studied, while the cellulose acetate membrane adsorbed less than the polyamide membrane. This can be explained by the fact that cellulose has practically no binding capacity for steroids [166, 167]. In the presence of natural organic matter a clear trend between hydrophobicity and adsorption of trace contaminants (e.g. hormones, analgesics, antibiotics, etc.) on polyamide active layers is not clear either [96].

In terms of retention of micropollutants by membrane polymers, generally, higher micropollutant hydrophobicity results in lower retention [34, 164, 168]. However, several studies showed that membrane rejection of organic compounds (including hormones, pharmaceuticals, pesticides, etc.) varies greatly for similar hydrophobicities [33, 36, 91, 169]. In the case of non-phenylic pesticides retention increased with increase of hydrophobicity for NF membranes with PA or PES active layers [100]. Comerton *et al.* [169] obtained a higher retention by a PA NF active layer for the DES hormone compared to the other hormones, despite DES being much more hydrophobic (see Table 1). Kim *et al.* [38] equally obtained higher retention values for more hydrophobic contaminants such as disinfection by-products and chlorinated solvents.

As can be seen in Figure 11 for contact angle and Figure 12 for log K_{OW}, this does not always correlate affinity with retention successfully. The reason being that hydrophobicity fails to identify specific material affinities between polymers and micropollutants [83]. It is therefore important to understand underlying adsorption mechanisms in more detail.

[Figure 11]

[Figure 12]

One of the main reasons why so little is known about membrane adsorption is the difficulty in obtaining specific material characteristics for membrane polymers. Some characterisation data is available, for example gas adsorption analysis conducted on PE showed that there was almost no internal porosity and the polymer had a small surface area compared to other particles. Nevertheless, partitioning was stated to play an important role in sorption atrazine and trichloroethene to PE which is a strongly hydrophobic polymer [150, 170]. Other authors attributed a slow diffusion of the hydrophobic compounds into PP granules to slow sorption [171].

When looking at more detailed chemical characteristics, results in Figure 10 showed that the absence of both double bonded oxygen and ring structure reduce sorption of estradiol. However, the PE based polymers such as PET and PEN do not readily adsorb estradiol despite having these functional groups. The difference in interaction might lie in the fact that PE have oxygen in the form of ketone groups (=O) and PES have oxygen in the form of sulphonyl groups ($-SO_2$). In the case of polyamide, despite the absence of a ring structure hydrogen bonding interactions are possible between the amine and the ketone group. Interestingly, polyamide (nylon 6) is used in thin

layer chromatography (TLC) to separate organic compounds that are able to hydrogen bond. In consequence, polyamide had been used for separation of phenols, carboxylic acids, amino acid derivatives, steroids, quinines, aromatic nitro compounds, nucleotides, bile pigments and pesticides [172, 173]. Beyond chromatography, such principles are used for sample pre-treatment such as solid phase extraction. Hydrophobic effect, dipole–dipole, dipole–induced dipole and dispersive interactions, hydrogen bonding and ionic interactions play role for the interactions between the analytes and the sorbent [174], with hydrophobic interaction being the most widely used sorption mechanism in solid phase extraction [175].

Hydrophobicity is clearly not the decisive factor in determining adsorption indicating that other types of interactions (supramolecular interactions such as hydrogen bonding and π-π stacking) may play an important role.

8 Supramolecular Mechanisms in Micropollutant Sorption by Polymers

Adsorption is dependent on the membrane material used [23, 100], the contaminant and its properties such as hydrophobicity [58, 60, 95, 96, 100, 111, 176], acid dissociation constant [95, 96, 111] and aptitude to hydrogen bond or engage in other supramolecular interactions.

A summary of such interactions, as described in supramolecular chemistry and adapted to possible micropollutant interactions is shown in Figure 13. A further example of such interactions are carbon based nanomaterials that have a high capacity for hydrophobic, electrostatic and π-π interactions [177]. In fact, Ji *et al.* [178] proposed that π-π interactions were responsible for the sorption of sulphonamide antibiotics on multiwalled carbon nanotubes. As many of such interactions are not yet well understood and very difficult to quantify, the occurrence and their extent of those interactions remains speculative.

[Figure 13]

The mechanism of possible hydrogen bonding interactions for a number of polymers is illustrated in Figure 14. In addition to H-bonding, π-π interactions are a possible mechanism to be considered. The difference between the π densities of the adsorbent and the corresponding adsorbate determines the stability of the π-π interaction. π density is determined by electron rich and deficient aromatic fragments [179].

[Figure 14]

Returning to characteristics summarised in Table 3 and results in Figure 10 a number of observations can be made. π-π interactions and strong hydrophobic interactions are involved in the sorption mechanisms of methylene and phenyl groups to hypercrosslinked polystyrene [180]. Davankov (2003) [179] states that π-π interactions between the hypercrosslinked polystyrene and the substances with π-systems of electrons such as aromatic rings, carboxyl groups and alike governs the retention mechanisms in HPLC application with non-polar solvents. In fact, hypercrosslinked polystyrene has a strong π-electron donating-accepting ability in non-polar organic solvents. This ability results in high sorption capacity of compounds which contain aromatic π-systems or functional groups with free electron pairs in HPLC application [181]. Sorbents used in SPE with phenyl groups (such as polystyrene divinlybenzene) have the capacity to interact with steroids through π-π interactions. The number and positioning of phenyl groups in this phase determine the level of π-π interactions and the sorption capacity. It was suggested that the π-π interaction between the phenyl phase and the steroid occurs when the double bonds of steroid and phenyl group overlap [182]. Similar phenomena are likely when estrogens are in contact with membrane polymers which may explain the strong sorption of estrogens by polystyrene, although the main mechanism for polystyrene sorption is hydrophobic interactions (Figure 10A). The aromatic ring in polystyrene is electron neutral, while the benzene rings in estrone and estradiol are

electron rich. For π-π interactions to occur an electron poor aromatic group is required in the polymer. In consequence π-π interaction is anticipated to not be a major contributing mechanism in this case. The extent and precise type of contribution is not possible to determine with currently available tools.

Polyamide is the strongest adsorbent of the polymers tested which can be explained by its quite polar nature and ability to act as both hydrogen acceptor and donor. Results obtained in estrogen sorption to the polymer confirm the observations in membrane filtration. In contrast, PVDF is considered a hydrophobic polymer but is known to dislike interactions with either with hydrophobic or hydrophilic compounds. The adsorption to PVDF (Figure 10B) is indeed relatively low.

Polysulphone (Figure 10A) and polyethersulphone radel (PES R, Figure 10B) have similar functional groups but the hormone sorption onto these polymers is very different. This difference can be explained by the fact that polysulphone has more diluted functional groups in the structure compared to PES R. The sulphone group of PES R makes the polymer polar and available for H-bonding.

Although cellulose has a high capacity for H-bonding it does not like to H-bond with other molecules which is confirmed with the estrogen results (Figure 10A). It does, however, interact with its own functional groups.

Clearly, polymer-hormone interactions cannot be explained by only one interaction mechanism. While the qualitative and quantitative measurement of such interactions is currently limited by the availability of suitable characterisation tools, the above results indicate that such interactions ay indeed play an important role in sorption. Supramolecular interactions such as hydrogen bonding involving micropollutants and polymers are weaker in nature and quantification of both interaction energy and identification of specific mechanisms is currently limited to molecular dynamics simulations. This limits the predictive capacity of membrane models that accurately predict both retention and sorption.

9 Conclusions & Outlook

The aim of this review has been to illustrate the impact of adsorption of micropollutant retention in membrane filtration and to elucidate mechanisms of micropollutant adsorption to membrane polymers. Estrogens were used as an example of such micropollutants. Interaction mechanisms are governed, most likely, by hydrophobic as well as solvation effects and interplay of molecular and supramolecular interactions such as hydrogen bonding, π-cation/anion interactions, π-π stacking, ion-dipole and dipole-dipole interactions. The extent of which each mechanism contributes is naturally dependent on micropollutant and polymer characteristics. Besides such interactions, the available surface area of membrane polymers is the most important parameter. Challenges remain in the areas of; (i) qualitative and quantitative determination of chemical interactions between polymers and micropollutants, (ii) accurate characterisation of membrane material properties and internal surface area available for sorption, (iii) the integration of sorption phenomena into membrane retention models.

Systematic investigations are required to identify and quantify both relative contributions and strength of such interactions and develop suitable surface characterisation tools. This is a difficult endeavour given the complexity of systems, the possibility of several interactions taking place simultaneously and the generally relatively weak forces involved. Further developments in supramolecular chemistry to understand and measure complex interactions, surface analytical tools to quantify such interactions, molecular dynamics modelling and the availability of well defined membrane materials (such as carbon nanotube materials) will contribute significant progress in this field. With such enhanced understanding the design of membranes able to remove micropollutants over the range of characteristics will be possible.

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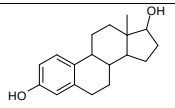
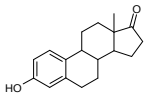
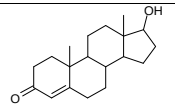
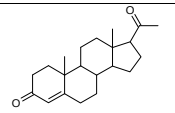
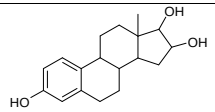
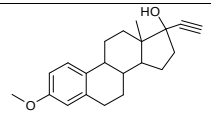
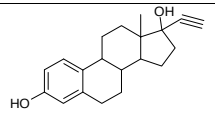
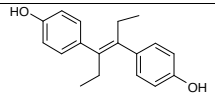
Table 1 Characteristics of micropollutant group of estrogens

Compound	Molecular Formula	CAS No.	Mol Structure	MW (g/mol)	Solubility in water (mg/L)	pK_a	Log K_{ow}	Dipole moment (Debye)	H bond capacity
Estradiol E2	$C_{18}H_{24}O_2$	50-28-2		272	3.6, 82 [b,f,s]	10.23 [c]	4.01 [g]	2.2 [h]	Strong OH donor and acceptor; π weak acceptor (benzene)
Estrone E1	$C_{18}H_{22}O_2$	53-16-7		270	13, 147 [f,l,s]	10.34 [c]	3.13 [g]	2.1, 3.36[h,o]	Strong OH donor and acceptor; Strong =O acceptor; π weak acceptor (benzene)
Testosterone T	$C_{19}H_{28}O_2$	58-22-0		288	24, 68[m,s]	17.4[s]	3.32 [g]	3.53[e]	Strong OH donor and acceptor; Strong =O acceptor; π weak acceptor (benzene)
Progesterone P	$C_{21}H_{30}O_2$	57-83-0		315	5, 8.8[m,s]	NA	3.87 [g]	3.50, 4.58[e,o]	Strong =O acceptor; π weak acceptor (benzene)
Estriol E3	$C_{18}H_{24}O_3$	50-27-1		288	13, 441[l,r,s]	10.25, 10.4[n,s]	2.60 [l]	1.71, 3.22[o,r]	Strong OH donor and acceptor; π weak acceptor (benzene)
Mestranol ME2	$C_{21}H_{26}O_2$	72-33-3		310	0.3, 3.5 [l,s]	-	4.10 [l]	-	Strong OH donor and acceptor; Strong -O- acceptor; π weak acceptor (benzene)
Ethinylestradiol EE2	$C_{20}H_{24}O_2$	57-63-6		296	4.8, 116 [r,s,l]	10.25, 10.5[n,s]	3.67 [l]	2.64[r]	Strong OH donor and acceptor; π weak acceptor (benzene)
Diethylstilbestrol DES	$C_{18}H_{20}O_2$	56-53-1		268	12[r]	-	5.07[r]	1.62, 2.2 [q,r]	Strong OH donor and acceptor; π weak acceptor (benzene)

[a] [58],[b] [34],[c] [183],[d] [184],[e] [113],[f] [78],[g] [185],[h] [186],[i] [41],[j] [95],[k] [59],[l] [187],[m] [188],[n] [189],[o] [190],[p] [52],[q] [191],[r] [169],[s] [192]

Table 2 Membrane characteristics determined experimentally and average active layer thickness obtained from the literature for five membranes used

	Pore Radius R_{pore} (nm)	Active Layer Thickness Porosity Ratio L / ε (µm)	Average Active Layer Thickness L (nm)	Total Estimated Surface Area of Active Layer (cm^2)	Porosity	References
BW30	0.32	6.01	250	2968	0.042	[117]
NF90	0.34	1.46	174	5529	0.119	[113]
TFC-SR3	0.38	1.59	114	1978	0.072	[118] [119] [120][a]
NF270	0.42	1.05	35	294	0.033	[113] [114] [115] [116]
TFC-SR2	0.52	2.45	67	361	0.027	[113]

[a] determined as average of TFC-S and TFC-SR2 membrane thicknesses due to absence of literature data

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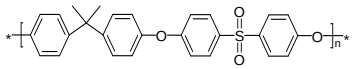
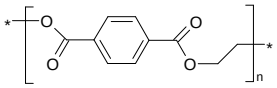
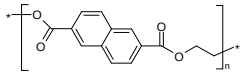
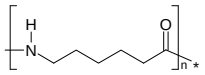
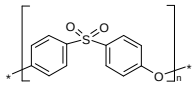
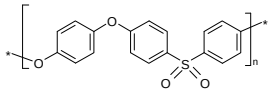
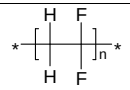
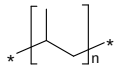
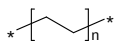
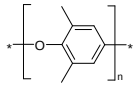
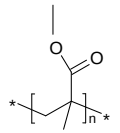
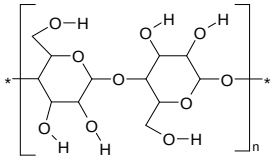
Table 3 Polymer type, supplier, and selected characteristics for polymer powders used in adsorption studies

Polymer Name	Supplier	Structure	Monomer Molecular Weight (g/mol)	Density [a] (g/cm^3)	Refractive Index (-)	Contact Angle (°)
Polysulphone (PSu), (PSu UDEL)	Goodfellow & Solvay		442	1.24	1.63[m]	77[c]
Polyester; Polyethylene Teraphthalate (PET)	Goodfellow		192	1.35	1.58-1.64[b]	79.09[d], 81[e], 70[f]
Polyester; Polyethylene Naphtalate (PEN)	Goodfellow		242	1.36	1.65-1.90	80[f]
Polyamide Nylon, 6 (PA)	Goodfellow		113	1.14	1.53[b]	70[e]
Polyethersulphone (PES)	Goodfellow		232	1.37	1.65[b]	56[g], 72[f]
Polyethersulphone (PES Radel A)	Solvay		324	1.37	1.65[b]	127[h]
Polyvinylidene fluoride (PVDF)	Solvay		64	1.78	1.42[m]	71[i]
Polystyrene (PS)	Goodfellow		104	1.05	1.59-1.60[b]	91[e]
Polypropylene (PP)	Goodfellow		42	0.9	1.49[b]	95[f]
Polyethylene (HDPE)	Goodfellow		28	0.95	1.54[b]	93-94[f]
Poly(2,6 dimethyl 1,4-phenylene oxide) (PPO)	Sigma		120	1.06	1.57[m]	88[j]
Polyacrylate; Poly(methyl methacrylate) (PMMA)	Sigma		100	1.2	1.49[m]	73[f]
Cellulose	Sigma		324	1.55	1.47[l]	24[k]

[a] Materials Safety Data Sheet, [b] [193], [c] [194], [d] [195], [e] [196], [f] [197], [g] [198], [h] [199], [i] [200], [j] [201], [k] [202], [l] [203], [m] [204]

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List of Figures

Figure 1 Steroid retention by different NF and RO membranes. The hormones represented are: estradiol E2 (272.4 g/mol), estrone E1 (270.4 g/mol), estriol E3 (288 g/mol), ethinylestradiol EE2 (296 g/mol), progesterone P (314.5 g/mol), testosterone T (MW=288.4 g/mol), mestranol ME2 (MW=310 g/mol) and diethylstilbestrol DES (MW=268.4 g/mol). The MWCO of the membranes varied between 100 and 560, data adapted from [34, 50, 52, 57, 63, 78, 94, 109, 110, 169, 176].

Figure 2 Micropollutant retention mechanisms in polymeric membranes A: Size Exclusion, B: Charge Repulsion, C: Adsorption, D: Sorption Diffusion, E: Solute-Solute Interactions, and F: Fouling Layer Interactions.

Figure 3 Estradiol filtration by NF270 membrane in MilliQ water at pH 7 and 11. A: Feed and permeate normalized concentration, B: Retention (%), C: Mass adsorbed (ng/cm^2) and D: Estradiol mass flux. The cross-flow conditions were 11 bar, Re 740, T 24°C, feed estradiol concentration 100 ng/L.

Figure 4 Estrone and Estradiol sorption and retention for several NF membranes as a function of pH. Membranes were not saturated prior to experiments (data adapted from [25, 63, 109, 110]).

Figure 5 Retention and mass adsorbed of estradiol per active (total) surface area and per membrane surface area (100 ng/L estradiol, 25°C, 11 bar and Re2800) of several polyamide on polysulphone membranes of increasing pore radius (BW30, NF90, TFC-SR3, NF270 and TFC-SR2, respectively).

Figure 6 Estradiol (E2), estrone (E1), progesterone (P) and testesterone (T) adsorbed on Electrodialysis; Anion Exchange (AEM) (Neosepta® AMX-SB) and Cation Exchange Membrane (CEM) (Neosepta® CMX-SB) (polymer material: Polystyrene Divinylbenzene, supplied by Eurodia, Germany; manufactured by ASTOM Corporation, Japan). Initial hormone concentration was 100 ng/L in 1mM$NaHCO_3$, 85.5 mM NaCl, pH 7 [122].

Figure 7 Mass estrone (E1) adsorbed by polystyrene nanoparticles with different particle size (46, 81, 465 and 3000 nm) for different MWCO UF membranes (regenerated cellulose active layer, polypropylene support layer). 1mM NaHCO3 buffer and 20mM NaCl electrolyte, pH 7, and 5 bar for 1, 3, 5 kDa. The mass of polystyrene used was 15.7mg/L. Filtration process took about 4.5, 3.5 and 2.4 h for 1, 3 and 5 kDa membranes, respectively. (Note that sorption is time dependent due to kinetics).

Figure 8 Total surface area of a hypothetical membrane as a function of thickness for several pore radius assuming cylindrical pores A) with 0.03 porosity, B) 0.1 porosity, C) 0.25 porosity. D) represents the surface area as a function of thickness of a membrane made of a cubic close packing formation of spheres with several sphere radius. The membrane surface area is 100 cm^2. The pore radius and thickness cover NF, UF and ED typical pore radius and thicknesses.

Figure 9 Electron-micrographs of the clean NF membranes A TFC-SR, B TFC-S, and C TFC-ULP illustrating enhanced polymer surface area due to surface roughness.

Figure 10 Estradiol adsorption to different pure and membrane polymer powders. A and B: Estradiol mass adsorbed/mass polymer, C and D: Estradiol mass adsorbed/polymer surface estimated from particle size measurements. 60 mL of 100 ng/L estradiol solution with 2.5g of Polymer, 6 ng initial estradiol mass, no background electrolyte. Filter was not saturated prior to the experiment and minimal losses were observed.

Figure 11 Estrogen adsorption as a function of polymer contact angle. Vertical line is the boundary between low wetting affinity (contact angle<90º) and high wetting affinity (>90º), as described by Mulder [162].

Figure 12 Adsorption of Estrone (E1), Estradiol (E2), Progesterone (P) and Testosterone (T) onto a Polyacrylate fibre and a NF270 membrane in filtration mode as a function of hormone log K_{OW} (data adapted from [54, 205]).

Figure 13 Selected possible polymer micropollutant interaction mechanisms. A Hydrophobic interaction between the membrane surface and estrone, B Hydrogen bonding between polyamide and estrone, C π-π interaction between aromatic rings of polystyrene and estrone, D Cation-π interation between the aromatic rings of estrone and functional group of polystyrene-divinylbenzene (Anion Exchange Membrane of electrodialysis membrane). Mechanisms adapted from [30].

Figure 14 Possible hydrogen bonding interactions between estradiol and polyamide, polysulphone, polystyrene and polydimethylphenyleneoxide (ppo). Bold arrows represent strong hydrogen interactions while the dotted arrows represent weak interactions. The head of the arrows point to H-bonding acceptors.

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Figure 1

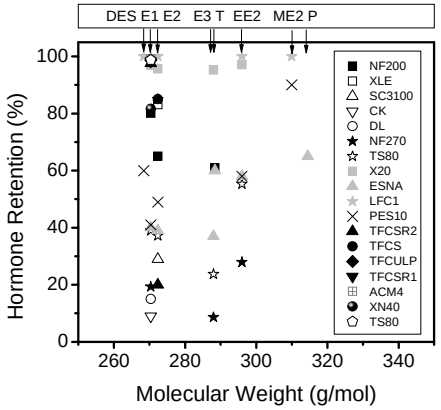

Figure 2

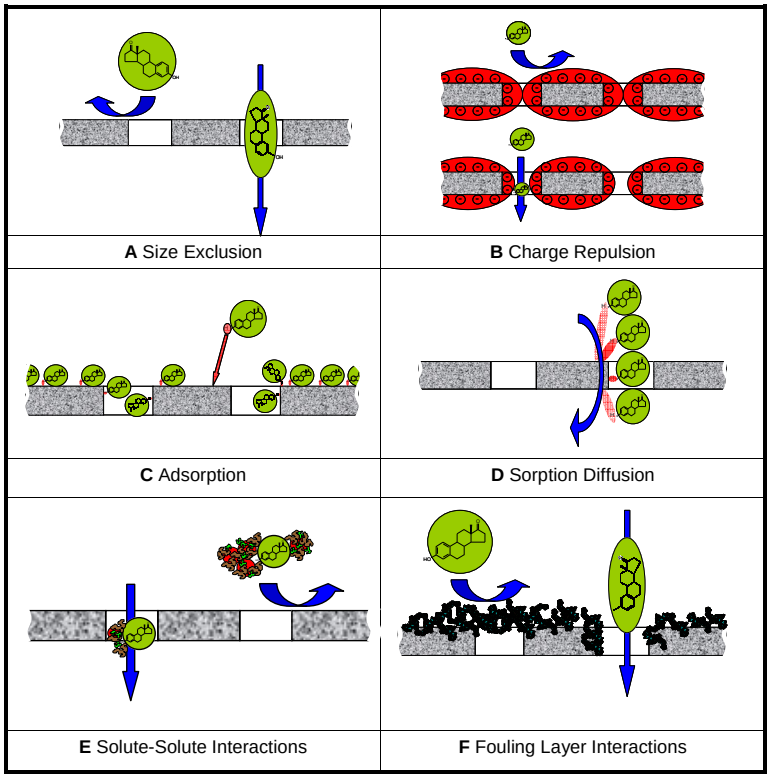

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Figure 3

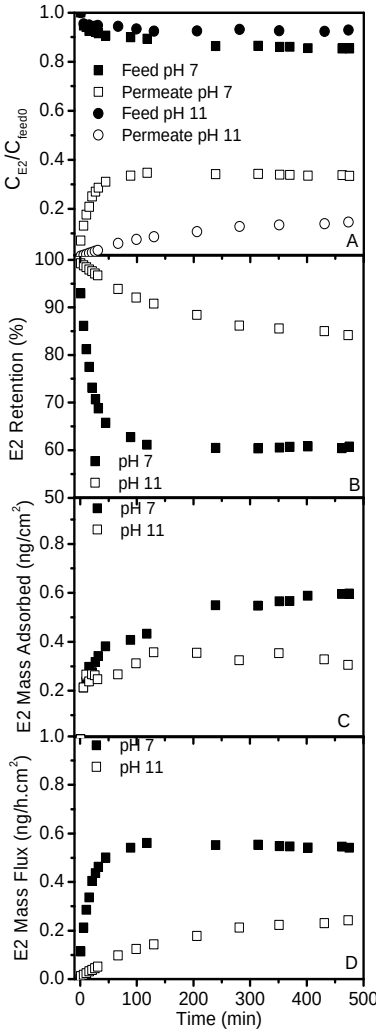

Figure 4

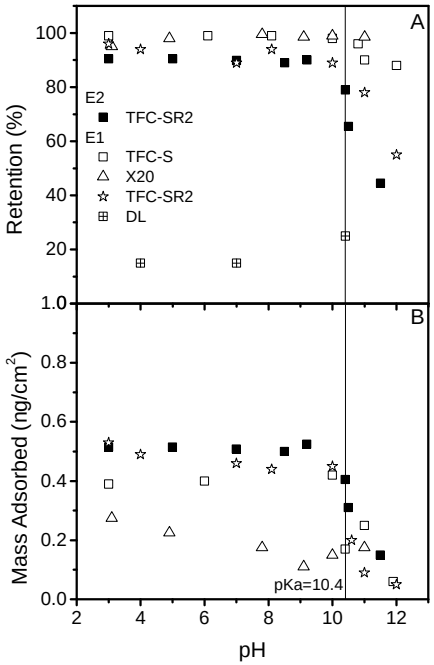

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Figure 5

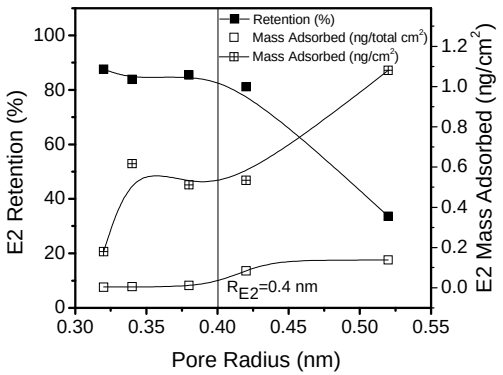

Figure 6

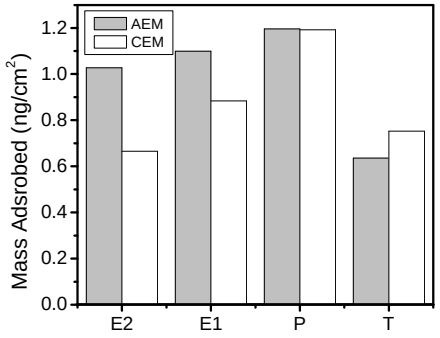

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Figure 7

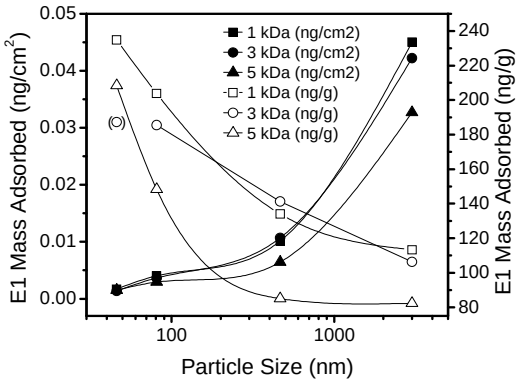

Figure 8

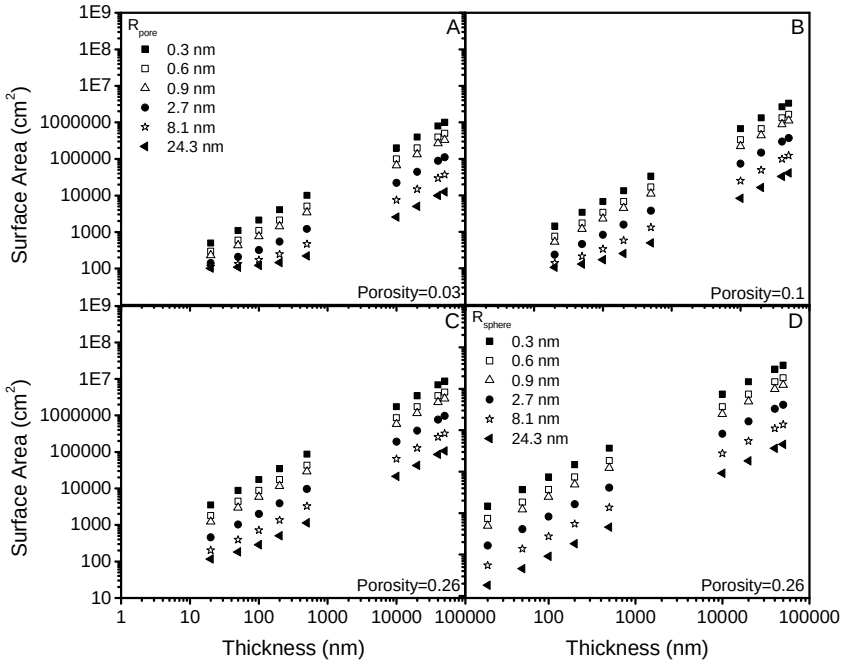

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Figure 9

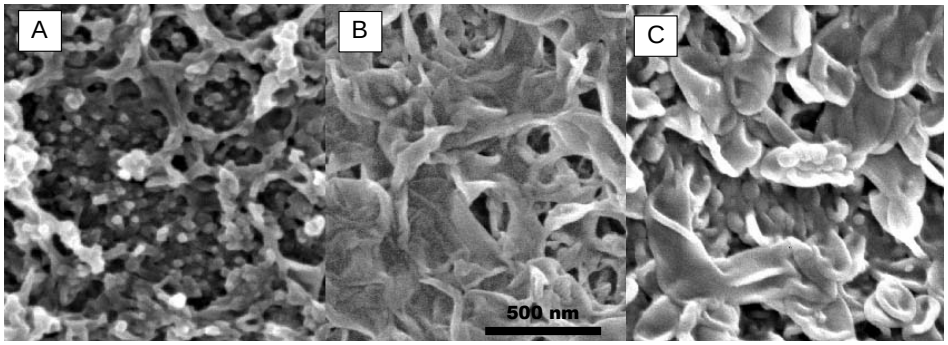

Figure 10

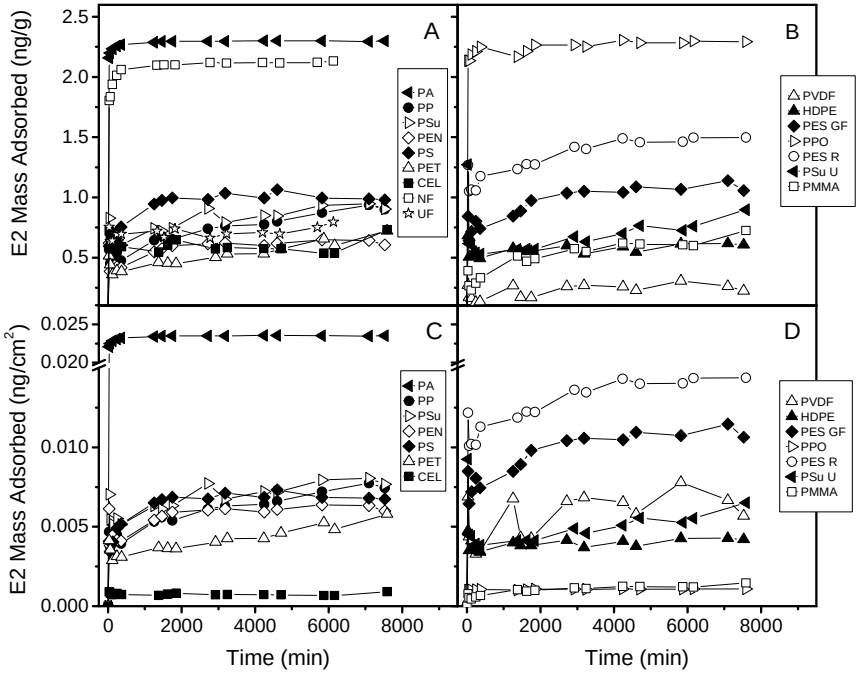

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Figure 11

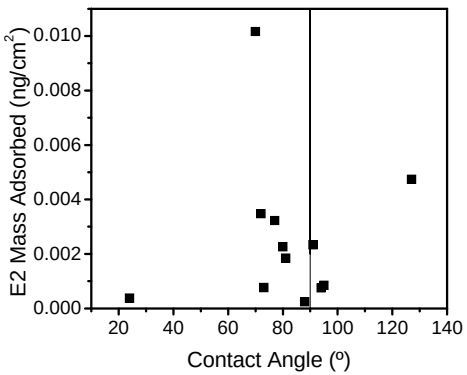
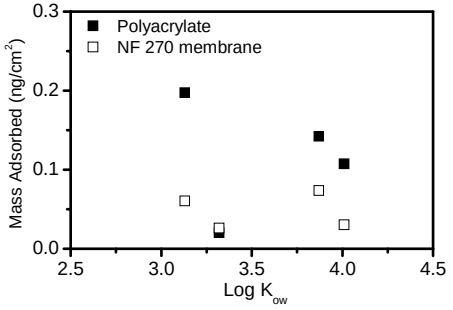
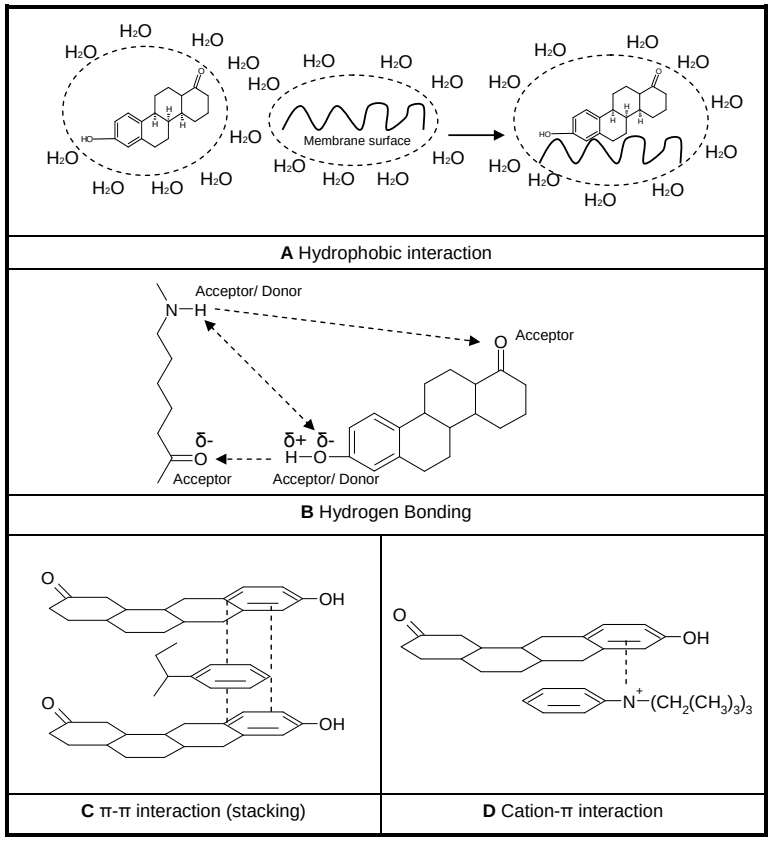


Figure 12



Schäfer, A.I. ; Semião, A. ; Akanyeti, I. (2011)
Micropollutant sorption to membrane polymers, Advances in Colloid and Interface Science, 'Membrane Separation and Colloid Science' invited special issue paper (accepted 09/2010).
doi:10.1016/j.cis.2010.09.006

Figure 13



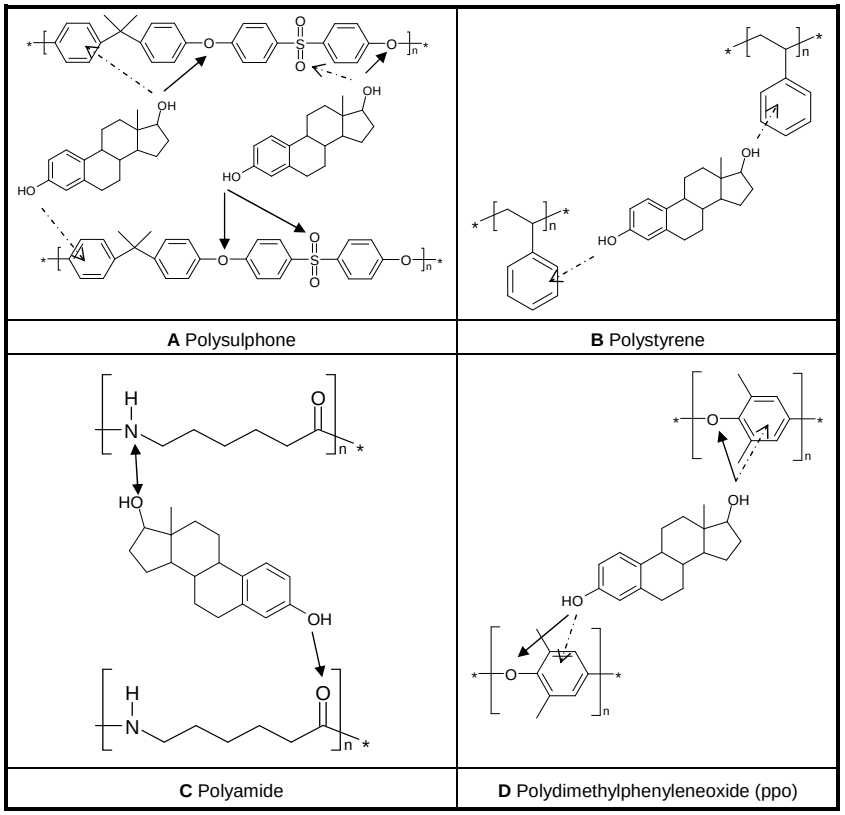
A Hydrophobic interaction

B Hydrogen Bonding

C π-π interaction (stacking)

D Cation-π interaction

Figure 14



A Polysulphone

B Polystyrene

C Polyamide

D Polydimethylphenyleneoxide (ppo)